Effect of Particle Size on the Hydrolysis of Parthenium Hysterophorus L. for the Production of Ethanol

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Abstract

Currently petroleum is being used as a major source for new chemicals, materials & fuels, although it has limitations in availability & costs. It also raises environmental concern. A promising alternative raw material for the production of bioethanol, a fossil fuel substitute, from renewable source is lignocellulosic biomass. Parthenium hysterophorus L, an obnoxious flowering, offers a big challenge to all attempts of control because of its high regeneration capacity, production of huge amounts of seeds, high seed germinabilty & extreme adaptability to wide range of ecosystems. Contact with this plant causes dermatitis & respiratory malfunction in humans, cattle and domestic animals due to the presence of the toxin "parthenin". In the present work Parthenium is hence chosen for the production of bioethanol. Conversion of hemicellulose, presented in the lignocellulosic biomass, into xylose is one of major steps, as it increases the quantity of reducing sugar which ultimately enhances the ethanol yield through fermentation process followed by saccharification of the available sugar. Hydrolysis and size of the biomass particles plays an important role in xylose production. The objective of this work was to study the effect of particle size on the yield of xylose, which is an important constituent of reducing sugar, from Parthenium hysterophorus during the hydrolysis process under specified conditions. The experiments were carried out with three different particle sizes (0.35 mm, 0.95 mm, 1.78 mm), at different sulphuric acid concentrations and treatment temperatures for 2 h soaking period. Maximum xylose yield was obtained from particle size of 0.95 mm.

Keywords

Parthenium; Lignocellulosic; Biomass; Particle Size; Xylose.

Introduction

Fossil fuels are fuels formed by natural processes such as anaerobic decomposition of buried, dead & decaying organisms. They are non renewable resources & production & use of fossil fuels raising environmental concerns. The ozone layer is being depleted because of green house gases emitted from these fuels. Therefore government around the world is seeking the use of indigenous biomass, a readily available & renewable source, not only for energy supply security but also as a means to support the local economy.

Bioethanol can effectively be used as a substitute for petroleum. It is already commonly used to increase octane Number and improve the emissions quality of gasoline in a 10% ethanol / 90% gasoline blend. Its energy density is higher than some of other alternative fuels, such as methanol, which means less volume is required to go to the same distance. Ethanol is also suitable for use in future fuel cell vehicles (FCVS) which would double the fuel efficiency [Marzialetti T., 2008]. Ethanol can be derived from food crops including grain, sugar beet and oil seeds. But they have certain limitations: a) It contributes to higher food prices due to competition with food crops, b) are an expensive option for an energy security taking into account total production costs excluding government grant and subsidies, c) also it provides only limited greenhouse gas reduction benefits and can result in accelerated deforestation. Many of the problems

associated with the food crops can be addressed by the production of ethanol manufactured from agricultural and forest residues and from non foodcrop feedstock like corn stover. But production of ethanol from corn stover leads to a competition with feedstock of animals; high costs of productions are a fundamental barrier to deployment; current harvesting, storage and transport systems are imperfect for processing and distributing biomass at the scale needed to support significance production of large volume [Huber G.W., 2007]. A promising alternative to ethanol production is the conversion of lignocellulosic biomass by hydrolysis & subsequent fermentations [Hamelinck C.N. et al, 2005]. Lignocellulose is the botanical term used for biomass from woody or fibrous plant materials, being a combination of lignin, cellulose and hemicellulose polymers interlinked in a heterogeneous matrix. The combined mass of cellulose and hemicellulose in the plant material varies with species but is typically 50-75% of the total dry mass with the remainder consisting of lignin. Cellulose is a linear homopolymer of anhydrous D-glucose units linked together by 1, 4 glucosidic bonds. Hydrogen bonding between cellulose molecules results in the formation of highly ordered crystalline regions that are not readily accessible to water. It is a straight chain polymer containing six carbon atoms. Hemicellulose is a heterogeneous material which is primarily a polymer of xylose and arabinose both being five carbon sugars. The hemicellulose forms hydrogen bonds with the cellulose microfibrils, increasing the stability of the cellulose–hemicellulose–lignin matrix. Lignin is composed of phenolic compounds that may act as an inhibitor to the hydrolysis or fermentation of sugars. It functions as a binding and encrusting material. The combination of hemicelluloses and lignin provide a protective sheath around the cellulose, which must be modified or removed before also the crystalline structure of cellulose makes it highly insoluble and resistant to attack. Therefore to economically hydrolyze (hemi) cellulose, more advanced pretreatment technologies are required than processing sugar or starch crops. Advantages of lignocellulosic biomass include: a) biomass derived hydrocarbon fuels are energy equivalent to fuels derived from petroleum. b) hydrocarbons from lignocellulosic biomass are immiscible in water, they are self separate, which eliminates the need for an expensive, energy-consuming distillation step, c) biomass derived hydrocarbon fuels are produced at high temperatures, which allows for faster conversion reactions in smaller reactors. Thus, processing units can be placed close to the biomass source or even transported on truck trailers, d) amount of water needed for processing hydrocarbon fuels from biomass can be greatly reduced [Jacobsen S.E., and Wynan C.E., 2002].

Improvement of the hydrolysis of lignocellulosics is a challenging task because of the recalcitrant of the material. A number of parameters like selection of raw material, size of feed particle, pretreatment time as well as concentration of H_2SO_4 have an effect on the hydrolysis of lignocelluloses. In this work, the focus was on the effect of particle size on the hydrolysis of Parthenium hysterophorus l. for the production of ethanol.

Parthenium hysterophorus is available in 4 continents in abundance. Their industrial processing costs are low and devoid of any environmental hazards. The increased utilization of P. Hysterophorus biomass as energy source and raw materials is necessary in the long term as fossil fuels are limited. Isolation andchemical investigation of the compounds in P. hysterophorus are required to decipher their properties and predict their applications. In this regard it is touted to become a boon for the human beings, animals and crops in near future.

Isolation and chemical elucidation of the active principles of P.hysterophorus is required to determine their chemical properties [Howard R.L. et al, 2003]. Chemical analysis of P.hysterophorus has indicated that all its parts including trichomes and pollen contain toxins called sesquiterpene lactones. P.hysterophorus contains a bitter glycoside parthenin, a major sesquiterpene lactone [Patel S., 2010]. Other phytotoxic compounds or allele-chemicals are hysterin, ambroisin, flavonoids such as quercelogetin, 3-7-dimethylether, 6-hydroxyl kaempferol, fumaric acid, vanilliic acid, aniscid acid, p- aniscisacid & some unidentified alcohol [Fayle T. et. al. 2007, Eberts T.J.et.al. 1979,].

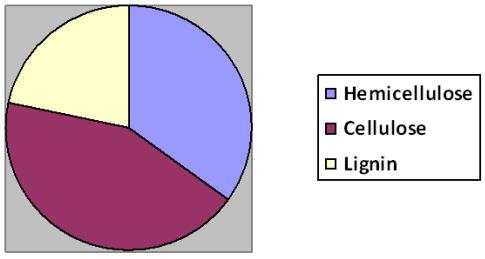

FIG.1 MAIN COMPONENTS OF *P. hysterophorus* USED IN THIS STUDY

FIG. 1 shows that P.hysterophorus has a high content of cellulose and hemicellulose. To make the hemicelluloses more accessible to acid, the biomass was pretreated under variable conditions.

Materials and Methods

Preparation of Parthenium for experiment

Fresh Parthenium with long stem was collected from local area. The Parthenium was thoroughly washed several times with tap water to remove adhering dirt, chopped into small pieces of size 1-2 cm (approx), and further grounded to even smaller particles of size 3-5 mm (approx), and finally dried in a hot air oven at 106^0C for 6 h. The dried material was stored at room temperature until used.

Preparation of Hemicellulose Acid Hydrolysate

1 g of dried Parthenium was mixed with 1%, 3% & 5% concentration sulfuric acid respectively to a final volume of 10 mL. The mixtures were soaked for 1h and 2hs for each set of sample. The acid hydrolysis reactions were carried out in the temperature range of 190°C, 210°C and 230°C for a treatment time of 2 min, 6 min and 10 min, after which the hydrolysate was cooled down to room temperature. The hydrolysate was filtered using Wattman paper no.1 to remove the unhydrolysed material and solid residue. The filtrate was collected and subjected to analyze the xylose content.

Determination of Xylose Content by Phloroglucinol Assay

Xylose content was determined using the Phloroglucinol assay [Johnson B. et.al., 1984 Pronyk C. et.al., 2010] with the hydrolysate obtained from acid hydrolysis. The colouring reagent mixture was heated in water bath and rapidly cooled to room temperature before measuring in a Spectrophotometer at 554 nm.

Benzoic Acid Solution Preparation

0.2 g of benzoic acid is mixed in 100 mL of distilled water, which was preheated at 60 ^{0}C, and mixed well, then cooled and filtered to store the solution.

D-xylose Preparation

D-xylose was dissolved in benzoic acid to prepare a xylose solution. 0.05 g of D-xylose were mixed with 10 mL of benzoic acid to prepare xylose solution (10 g/L) though the following methods.

100 mL of distilled water is heated.

i. 0.2 mg of benzoic acid GR (Guaranteed Reagent) is added slowly to the water.

ii. The solution is mixed thoroughly and filtered to remove the benzoic acid crystals.

iii. Stock solution of D-xylose is made by adding 0.05 g of

D-xylose in 10 mL benzoic acid solution.

From this stock, D-xylose solution of 0.4 g/L, 0.8 g/L, 1.2 g/L, 1.6 g/L and 2.0 g/L concentration D-xylose was prepared for the standard curve measured at 554 nm in UV-spectrophotometer.

Phloroglucinol Solution

To make 100 mL of Phloroglucinol solution, 100 mL of glacial acetic acid and 0.50 g of phloroglucinol were mixed together.

Measuring of Xylose

To measure xylose, 200 µL of sample was mixed with 5 mL of phloroglucinol solution for making the final mixture. The samples were heated at 100^0C for 4 min and cooled to room temperature. The samples were then measured with spectrophotometer and the absorbance was recorded at 554 nm.

Preparation of blank

2 mL of benzoic acid was added to 300 mL of $ZnSO_4$, 300 mL of NaOH, & 500 mL of concentrated HCl, then 5 mL of phloroglucinol solution was added to make the final mixture. The samples were heated at 100 ^{o}C for 5 min and cooled to room temperature.

Governing Equation

In mid 1940s, Saeman [Roberto I.C. et. al.,1994] modelled the first-order homogeneous kinetics of wood cellulose. Saccharification and it became the pioneer model for describing sugar degradation followed by hemicellulose hydrolysis. Monophasic hydrolysis of hemicellulose is described [Elander R .et.al., 1995] in a very simple way as equation 1:

$$\text{Hemicellulose} \xrightarrow{k_1} \text{Xylo-oligomers (O)} \xrightarrow{k_2} \text{Xylose (X)}$$
$$\xrightarrow{k_3} \text{Degradation Products (D)} \quad \text{--- (1)}$$

Where, k_1, k_2 & k_3 are the reaction rate constants of the respective reactions. The governing equations for hemicelluloses hydrolysis [12] are shown in TABLE 1.

TABLE 1 GOVERNING EQUATIONS FOR HEMICELLULOSE HYDROLYSIS

Monophasic Hydrolysis
$\frac{dH}{dt} = -k_1[H]$
$\frac{dO}{dt} = k_1[H] - k_2[O]$
$\frac{dX}{dt} = k_2[O] - k_3[X]$

Where, [H], [O] and [X] signify the concentration of hemicellulose, oligomers and xylose respectively.

Results and Discussion

Earlier work for the production of ethanol from parthenium is limited. The present work illustrates on the effect of the size of biomass particles for xylose conversion from hemicelluloses derived from Parthenium hysterophorus L. Successful bioconversion of lignocelluloses from locally available Parthenium to xylose production has been achieved by using dilute acid hydrolysis process. Hydrolysis of Parthenium by dilute acid yields mixture of sugars with xylose as a major component [Pessoa Jr A.et. al.,1997].

The effects of various sized biomass particles at a particular soaking time, treatment temperature and different concentrations of sulphuric acid on the xylose yield from hemicelluloses derived from Parthenium have been investigated and represented through FIG. 2-4. S_1, S_2 and S_3 represent 0.035 mm, 0.95 mm and 1.78 mm sized Parthenium biomass particles respectively.

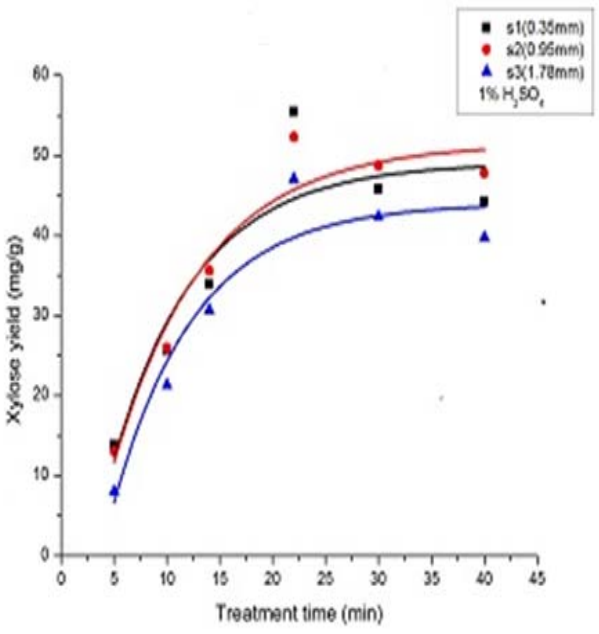

FIG. 2 EFFECT OF XYLOSE YIELD AT VARIOUS TREATMENT TIME USING S_1, S_2 AND S_3 BIOMASS PARTICLE SIZES AT 190 ^{0}C, 1% H_2SO_4 SOLUTION

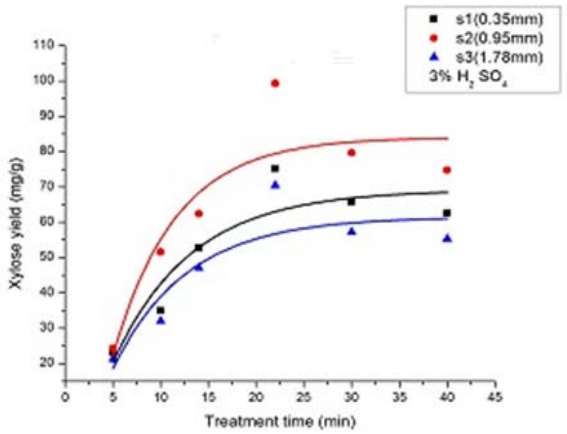

FIG. 3 EFFECT OF XYLOSE YIELD AT VARIOUS TREATMENT TIME WITH S_1, S_2 AND S_3 BIOMASS PARTICLE SIZES AT 190 ^{0}C, 3% H_2SO_4 SOLUTION

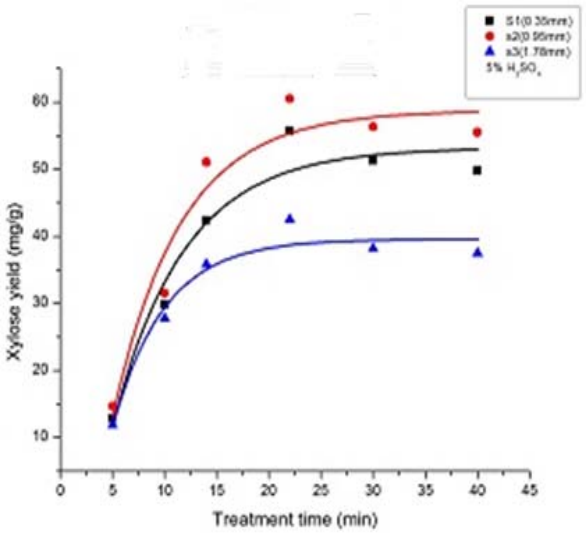

FIG. 4 EFFECT OF XYLOSE YIELD AT VARIOUS TREATMENT TIME WITH S_1, S_2 AND S_3 BIOMASS PARTICLE SIZES AT 190 ^{0}C, 5% H_2SO_4 SOLUTION

Thermodynamic of Acid Hydrolysis of Biomass

To evaluate the activation energy, the relationship between rate constant and temperature is utilized. The plot is called Arrhenius plot and is shown in FIG. 5-7. The energy of activation for the acid hydrolysis was studied at the temperature ranging from 423-483K. The activation energy obtained for various particle

sizes at various concentration of sulphuric acid is mentioned in TABLE 2-4. The frequency factor can be obtained from the intercept of the Arrhenius plot. The value of frequency factor indicates the collision of reactant molecules taking place with that frequency.

The free energy of activation (ΔG) for acid hydrolysis of biomass is obtained by using the equation:

$$\Delta G=\Delta H-T\Delta S \quad \text{--- (2)}$$

While the equilibrium constants for the acid hydrolysis are evaluated using the equation:

$$\Delta G = -RT\ln K \quad \text{--- (3)}$$

Where ΔH is enthalpy of activation, *R* is molar gas constant, ΔS is entropy of activation and K is the equilibrium constant respectively

The calculated values of ΔG, ΔH and ΔS for acid hydrolysis are mentioned in TABLE 5. Decrease in the value of entropy of activation with increase in temperature implies a stability of the products formed by the acid hydrolysis on the parthenium biomass. The increase in value of equilibrium constant, K with temperature also determines that the reaction's forward direction is favored.

TABLE 2: ARRHENIUS PLOT PARAMETERS FOR ACID HYDROLYSIS AT 1% H2SO4 FOR VARIOUS PARTICLE SIZES.

1/T(K^{-1})	lnk for s_1	lnk for s_2	lnk for s_3	s_1	s_2	s_3
0.00236	-0.678	-0.6333	-0.672	E_a (kJ/mol) 3.26	E_a (kJ/mol) 2.42	E_a (kJ/mol) 3.21
0.00225	-0.639	-0.595	-0.628			
0.00215	-0.590	-0.570	-0.592	A 0.25	A 0.055	A 0.24
0.00207	-0.568	-0.548	-0.559			

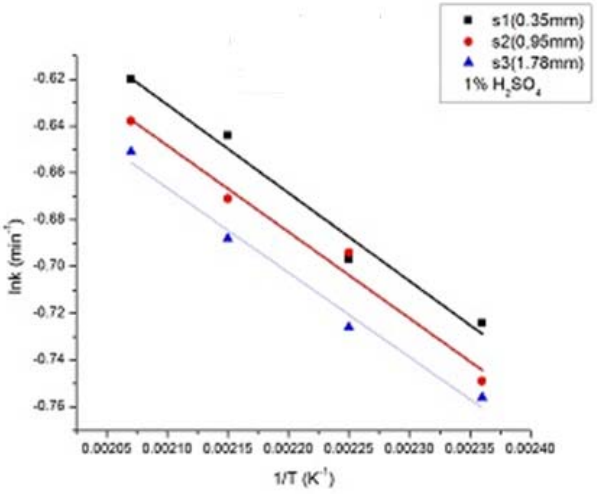

FIG. 5 ARRHENIUS PLOT FOR PARTHENIUM FEEDSTOCK WITH 1% H_2SO_4, lnk DATA FROM TABLE 2

TABLE 3 ARRHENIUS PLOT PARAMETERS FOR ACID HYDROLYSIS AT 3% H_2SO_4 FOR VARIOUS PARTICLE SIZES

1/T(K^{-1})	lnk for s_1	lnk for s_2	lnk for s_3	s_1	s_2	s_3
0.00236	-0.643	-0.667	-0.676	E_a (kJ/mol) 0.87	E_a (kJ/mol) 1.29	E_a (kJ/mol) 1.66
0.00225	-0.635	-0.646	-0.667			
0.00215	-0.623	-0.639	-0.641	A 0.39	A 0.3	A 0.21
0.00207	-0.613	-0.619	-0.619			

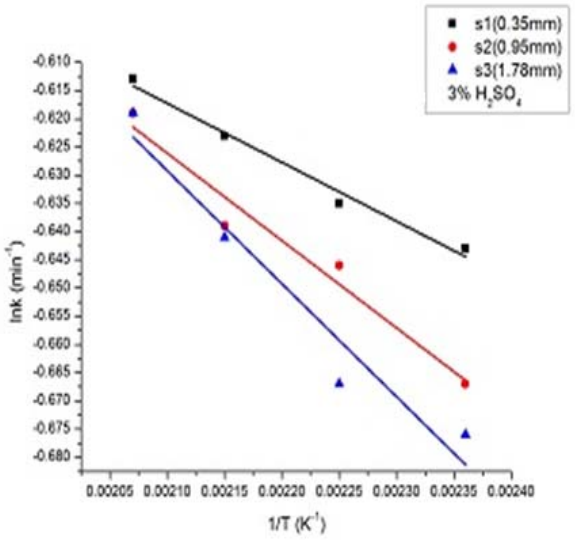

FIG. 6 ARRHENIUS PLOT FOR PARTHENIUM FEEDSTOCK WITH 3% H_2SO_4, lnk DATA FROM TABLE 3.

TABLE 4: ARRHENIUS PLOT PARAMETERS FOR ACID HYDROLYSIS AT 5% H_2SO_4 FOR VARIOUS PARTICLE SIZES

1/T(K^{-1})	lnk for s_1	lnk for s_2	lnk for s_3	s_1	s_2	s_3
0.00236	-0.7243	-0.749	-0.756	E_a 3.13	E_a 3.06	E_a 3.00
0.00225	-0.697	-0.694	-0.726			
0.00215	-0.644	-0.671	-0.688	A 0.15	A 0.12	A 0.1
0.00207	-0.620	-0.6378	-0.651			

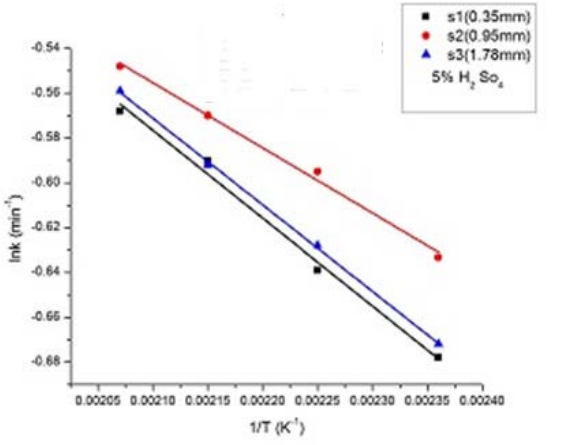

FIG. 7 ARRHENIUS PLOT FOR PARTHENIUM FEEDSTOCK WITH 5% H_2SO_4 , lnk DATA FROM TABLE AND ITS CORRESPONDING CURVES DESCRIBED BY BEST FITTED PARAMETERS.

TABLE 5 THERMODYNAMIC PARAMETERS FOR ACID HYDROLYSIS OF PARTHENIUM BIOMASS AT DIFFERENT PARTICLE SIZES

T (K)	1% H_2SO_4								
	ΔG (kJ/mol)			ΔH (kJ/mol)			ΔS (kJ/mol)		
	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3
423	2.83	2.22	2.36	3.21	2.3781	3.1829	0.002	0.00195	0.0019
443	2.35	2.19	2.31						
463	2.27	2.194	2.27						
483	2.28	2.20	2.24						
	3% H_2SO_4								
423	2.26	2.35	2.38	0.86	1.284	1.6862	-0.0033	-0.0025	-0.0017
443	2.34	2.38	2.46						
463	2.39	2.46	2.47						
483	2.46	2.49	2.49						
5% H_2SO_4									
423	2.55	2.63	2.66	3.11	3.0182	3.0092	0.0013	0.001	0.0008
443	2.57	2.56	2.67						
463	2.48	2.58	2.65						
483	2.49	2.56	2.62						

Conclusion

A comprehensive study of the effect of particle size on acid hydrolysis of Parthenium hysterophorus biomass was completed. The yield of xylose was compared by taking three different particle sizes (0.35 mm; 0.95 mm; 1.78 mm). Under the tested reaction conditions, xylose yield was highest for particle size 0.95 mm.

The physical structure of the feed such as surface area plays an important role in the yield of xylose. Hydrolysis of cellulose in plant and wood cell walls is expected to be affected by its chemical composition as well as structural and morphological features. Considering that particle size reduction opens up to some degree, the tightly structured cell wall and allows enzymes to access to the carbohydrate polymers, role of particle size reduction was investigated by hydrolyzing three different size fractions of Parthenium hysterophorus feedstock. The idea behind choosing three particle sizes was to see the effect of increased surface area on lignocellulosic hydrolysis. As particle sizes decreases, the ratio of surface area to mass grows enormously. This may provide many more reaction sites, i.e places where molecules can collide and interact. More collision from particles may make it easier to act faster, whereas in bigger particle most of the mass is inside and unavailable for reactions. Therefore for the bigger particle size (1.78mm), xylose yield is comparatively less. The experimental results showed that the optimum particle size was 0.95 mm at which maximum xylose yield was 99.304 mg/g of dry parthenium biomass at 190^0C temperature, 22 min treatment time and with 3% H_2SO_4 acid concentration, for 2 h soaking period.

Arrhenius parameters that described the measured reaction rates in the studied range of temperature and acid concentration were also developed.

Overall, this study presents a comprehensive view on the effect of particle size on hydrolysis of Parthenium, considering variable reaction parameters.

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